NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: OVERVIEW

DENNIS DEES

2016 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

Project ID ES261

OVERVIEW

Timeline

- Start: October 1, 2015
  - Kickoff: January, 2016
- End: September 30, 2018
- Percent Complete: 17%

Budget

- Total project funding:
  - FY16 - $4000K
- ES261 and ES262

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

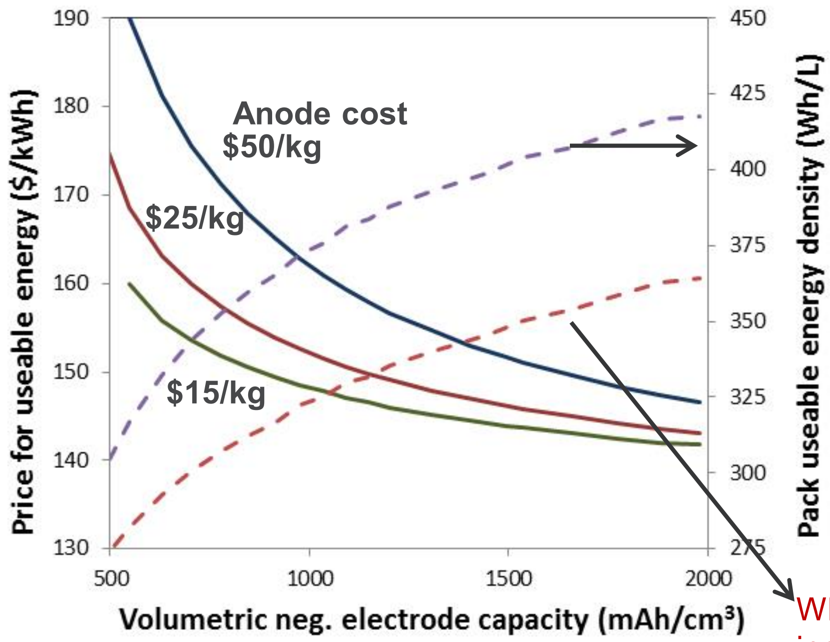
Partners

- Sandia National Laboratories
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

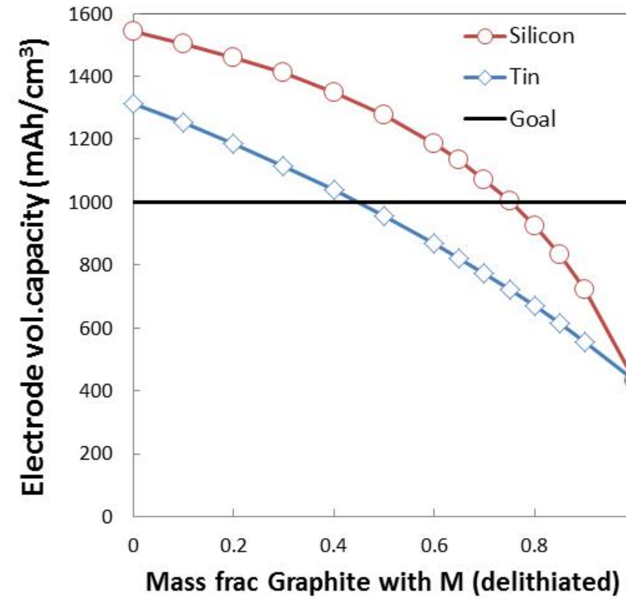
Battery Performance and Cost (BatPaC) Model Utilized to Establish Relevance by Connecting Pack to Anode Targets

- Pack level benefits reach diminishing returns after **1000 mAh/cm³** for both cost and energy density
  - mAh/cm³ [electrode basis] = $\rho \cdot \varepsilon \cdot Q$ [$g/cm^3_{act} \cdot cm^3_{act}/cm^3_{elect} \cdot mAh/g$]
- Silicon with <75 wt% graphite can achieve target



Wh/L including foam between cells 2x volume expansion

45 kWh$_{use}$, 90 kW 360 V
$20/kg 200 mAh/g NMC cathode



Electrode volumetric capacity uses lithiated basis $Li_{4.4}Si$ or $Li_{4.4}Sn$ and maximum active material volume fraction of 65%

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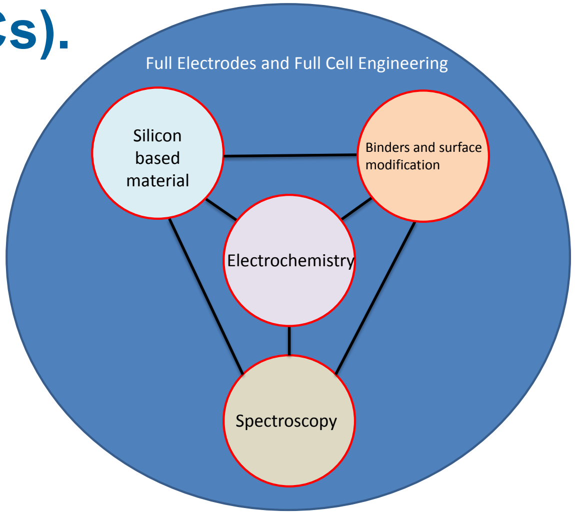
APPROACH

Initial Focus on Insights into and Advancement of Silicon-Based Materials, Electrodes, and Cells (SiBMECs).



- Stand-up program, based on expertise and past work:
  - Develop technical targets
  - Assign individual responsibilities
  - Initiate work
  - Establish communications
- Anode advancements verified based on life and performance of full cells.
  - Establish baseline SiBMECs and testing protocols.
  - Supported by Cell Analysis, Modeling, and Prototyping (CAMP) facility and Battery Manufacturing Facility (BMF)
- Plan and conduct a wide range of diagnostic studies on SiBMECs.
  - Establish structure-composition-property relationships.
  - Lithium-alloying surface and bulk transport and kinetic phenomena.
  - Assessment of failure modes.
  - Supported by Post-Test Facility (PTF)
- Evaluation of safety and abuse tolerance of SiBMECs.
  - Supported by Battery Abuse Testing Laboratory (BATLab)

APPROACH (CONTINUED)

As the Program Matures, Materials Developments will be Incorporated into Baseline SiBMECs.

- Materials development on SiBMECs to enhance interfacial stability, accommodate intermetallic volume changes, and improve overall performance and life.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals: $Me_xSi_{0.66}Sn_{0.34}$ (Me: Cu, Ni, Fe, Mn).
  - Examine a wide range of functional binders.
  - Interfacial modifications: MLD/ALD, surface coatings, and electrolyte additives.
- Materials advances can be scaled-up with the support of the Materials Engineering Research Facility (MERF).
- Materials advances will be incorporated into baseline SiBMECs with support of BMF and CAMP facility.
- Communicate progress to battery community.
  - Open to industrial participation and/or collaboration that does not limit program innovation or the free flow of information

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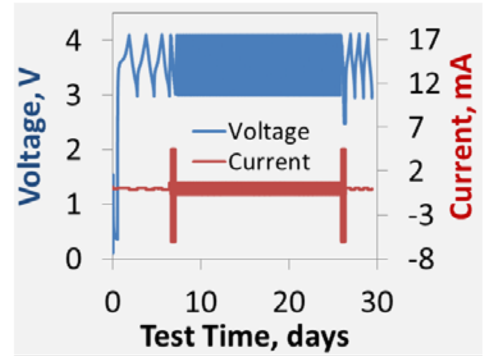
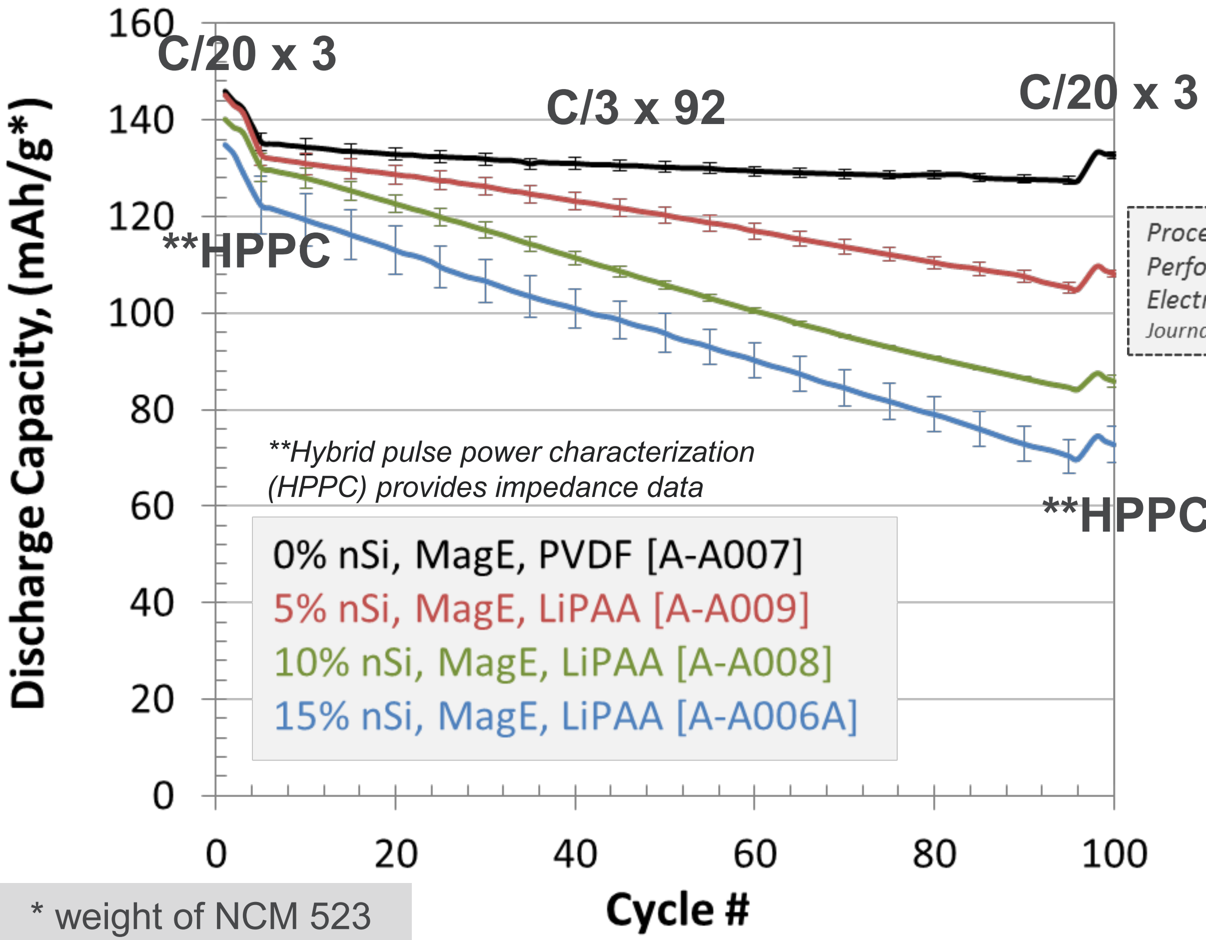
ADOPTED ELECTRODES AND PROTOCOLS FROM CAMP FOR INITIAL BASELINES



Full Baseline Cells Capacity Fade



* weight of NCM 523

Procedure reference:
Performance of Full Cells Containing Carbonate-Based LiFSI Electrolytes and Silicon-Graphite Negative Electrodes
Journal of The Electrochemical Society, 163 (3) A345-A350 (2016)

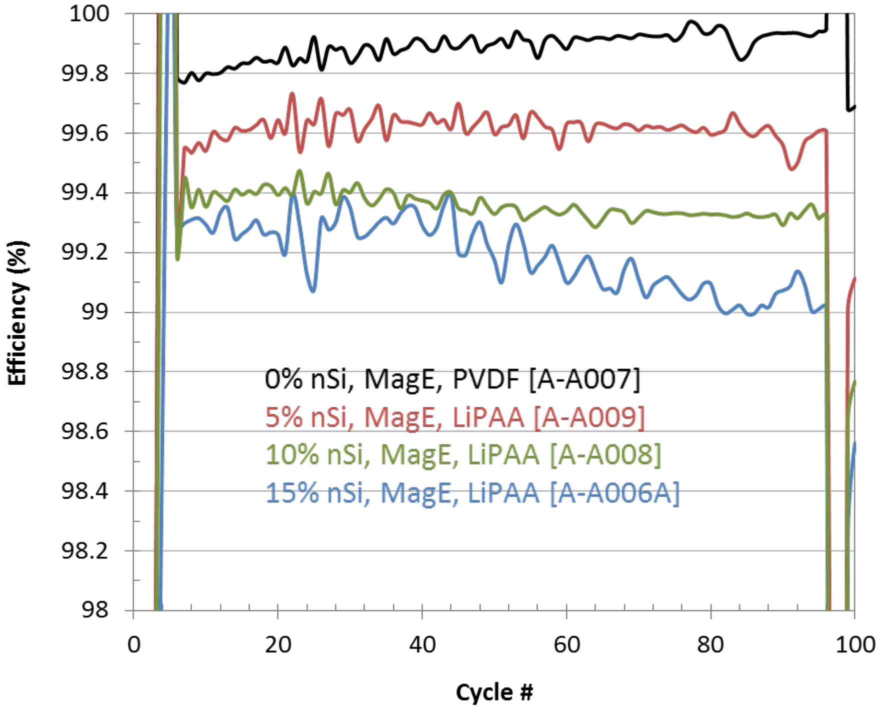
Cathode: A-C013A
90 wt% Toda NCM 523
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

Anodes: A-A00_
92-73 wt% Hitachi MagE
0-15 wt% Nano&Amor Silicon (50-70nm)
2 wt% Timcal C45
10 wt% LiPAA (LiOH titrate)

~2 mAh/cm^2 electrode couples
Single-sided
Matched to ~1.10 to 1.30 n:p ratio

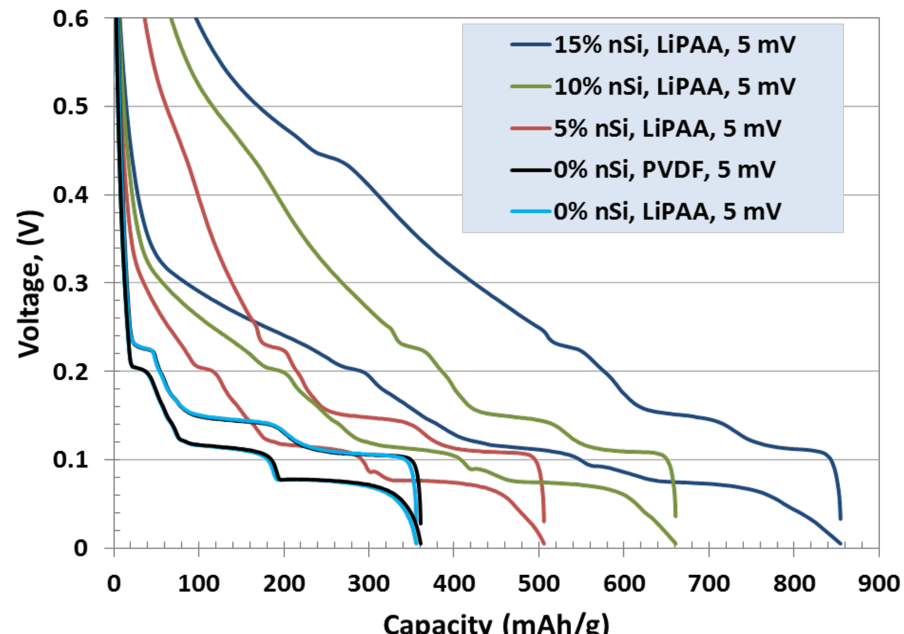
SILICON CONTENT HAS SIGNIFICANT IMPACT ON VOLTAGE PROFILE AND CURRENT EFFICIENCY

Full Baseline Cells Current Efficiency



As the Silicon content increases:
--- Specific energy increases
--- Increased voltage hysteresis
--- Lower current efficiency

Half-Cells Voltage Profile



- Strong correlation between plateaus in SiGr and Gr
- $Li_{15}Si_4$ presence in cells discharged below 50 mV

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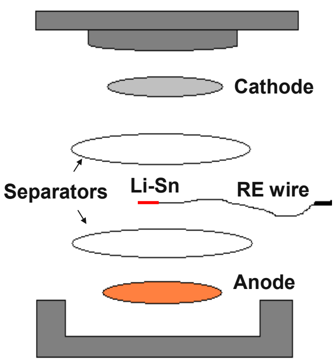
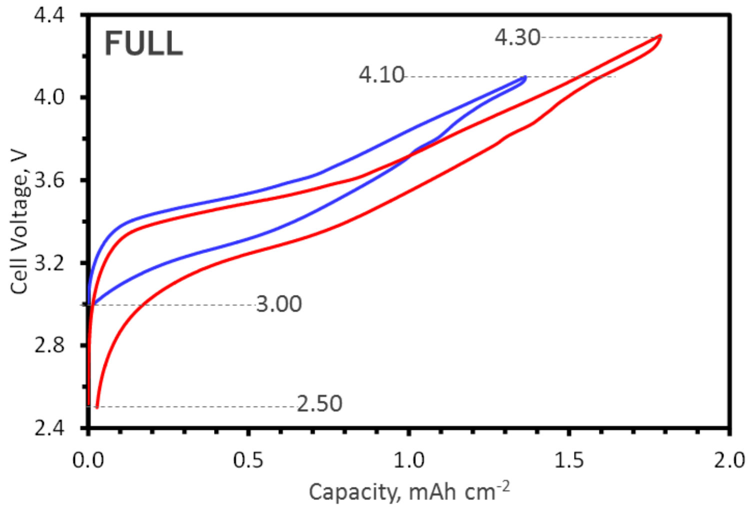
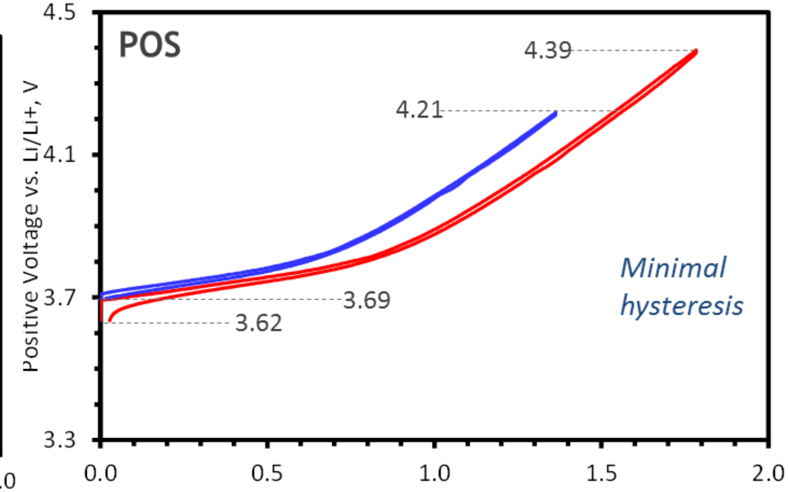
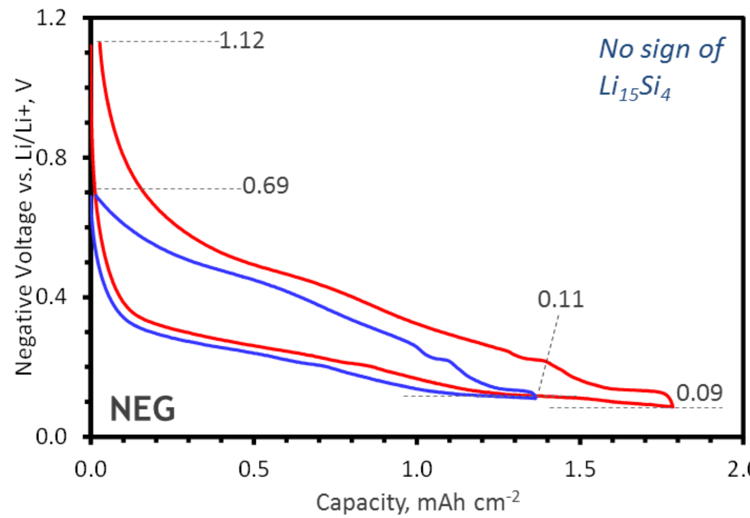
ELECTROCHEMICAL INVESTIGATIONS INCLUDE REFERENCE ELECTRODE STUDIES

Baseline NCM523/SiGr, Li RE, ~C/30, 2.5-4.3 & 3-4.1 V voltage windows









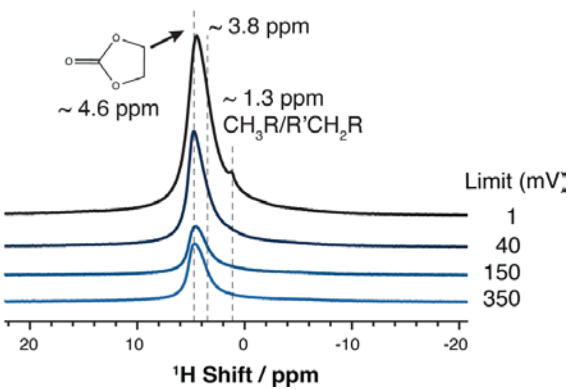
For cells discharged to 2.5 V, 10% of capacity is between 3 & 2.5 V. However, at a cell voltage of 2.5 V, the negative electrode potential is 1.12 V, which increases the likelihood of SEI decomposition and gas generation. Limiting LCV to 3.0 V improves cell life.

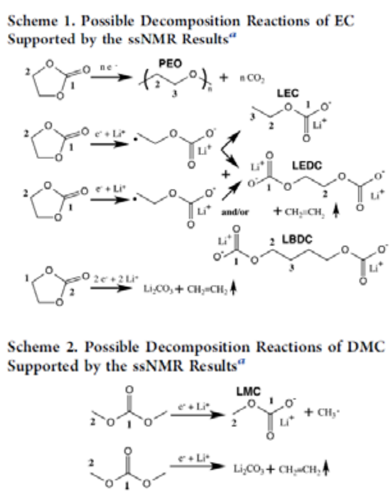
USING NMR SPECTROSCOPY TO STUDY SILICON AND INTERMETALLIC ELECTRODES

ex-situ Multinuclear MAS NMR, *in-situ* NMR and Solutions NMR

- ^{7}Li and ^{29}Si NMR have been used to reveal entire Li-Si reaction mechanism
- ^{7}Li-^{29}Si-^{1}H-^{19}F-^{13}C MAS NMR correlation experiments have been used to understand SEI formation, nature of degradation products and other reactions in a silicon based electrode.
- It is possible to effectively study anode SEI and amorphous Li_xSi composition both qualitatively and quantitative via NMR studies on silicon and other intermetallics electrodes

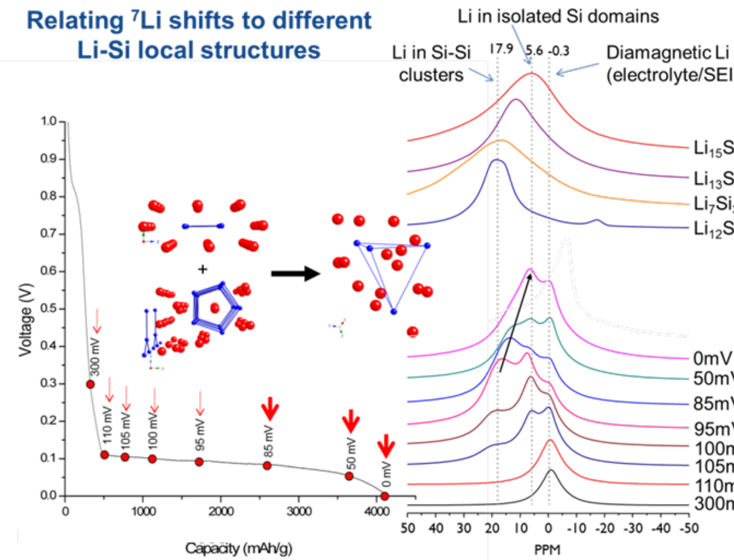
Determination of organic decomposition products





Michan *et al, Chem. Mater.,* 2015

Relating ^{7}Li shifts to different Li-Si local structures



Key *et al.* JACS, 2009

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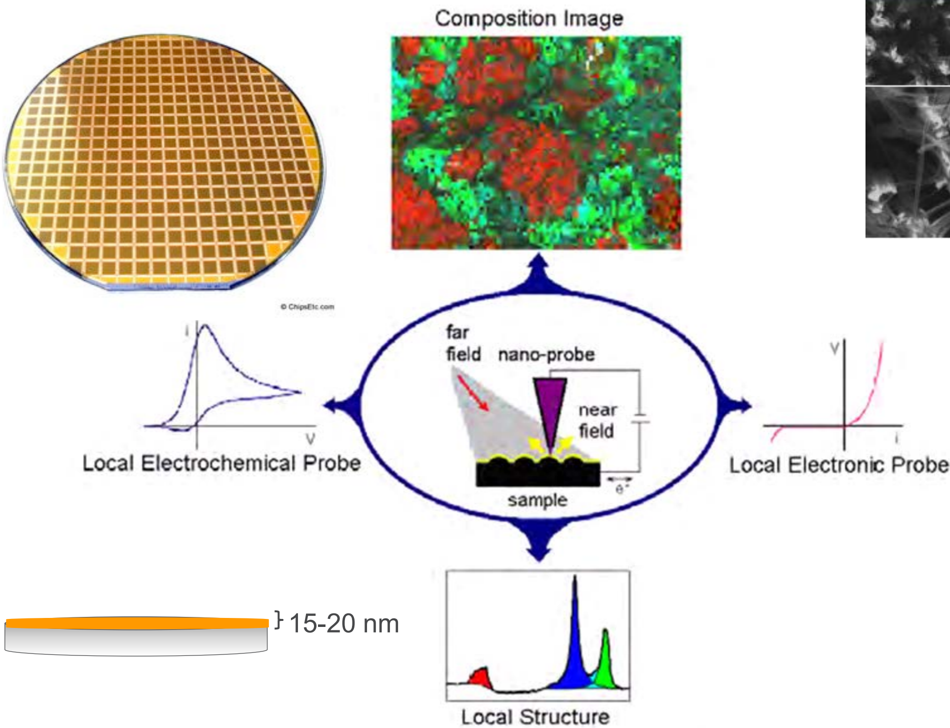
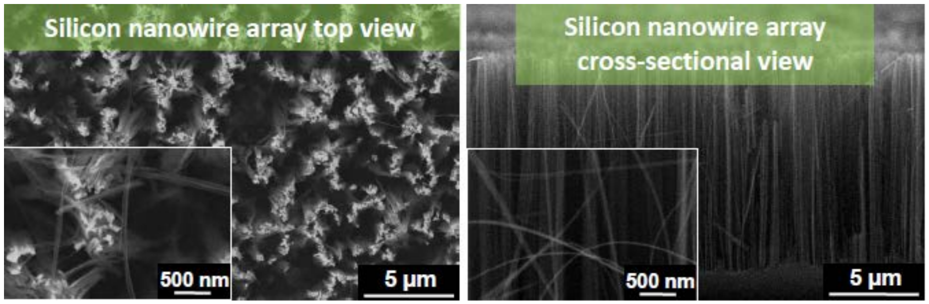
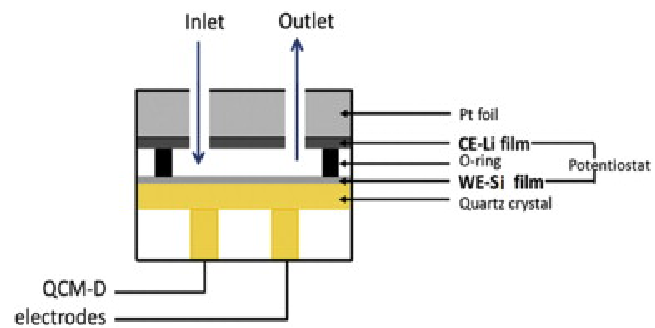
DIAGNOSTIC STUDIES OF MODEL SILICON-BASED ANODES

ES262

Characterization Studies on Thin Film Si, Si/C, and Si/Binder Electrodes; also Silicon Nano-Wire Electrodes







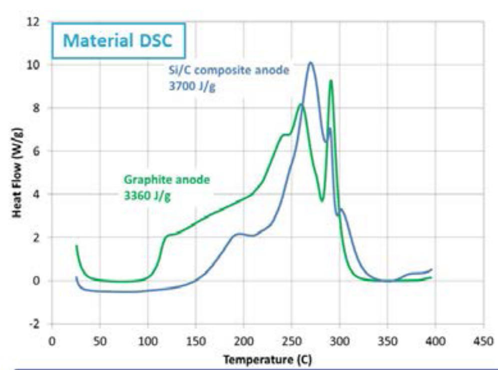
Schematic diagram of the experimental arrangement for EQCM-D measurements

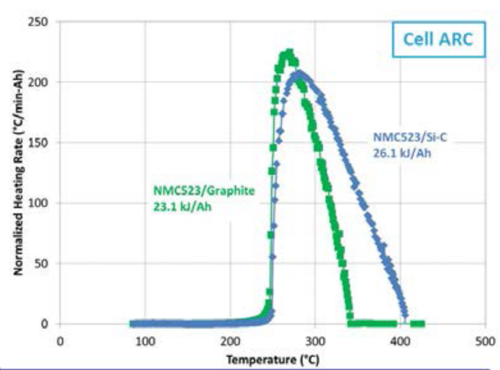
- Apply electrochemical, *ex-situ* and *in-situ* optical, X-ray, and neutron probes capable of sensing surface layers at a submonolayer sensitivity and resolution
- Study *in situ* surface mass changes of electrodes during electrochemical processes

EVALUATION OF SAFETY AND ABUSE TOLERANCE OF SILICON ELECTRODES

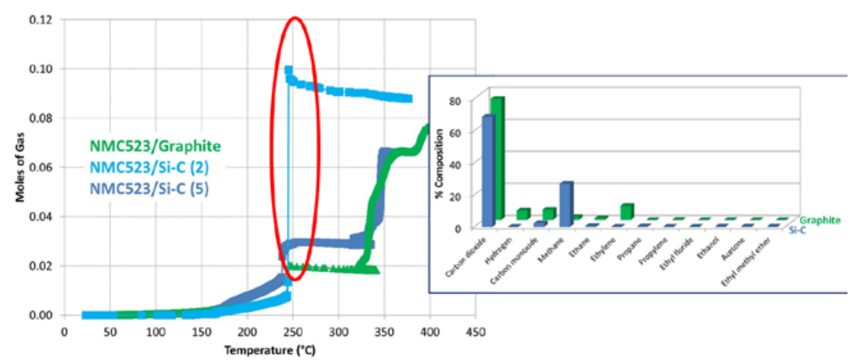
Initiated Studies on Electrodes and Cells

- The reactivity with silicon-based anodes under abuse is largely unknown.
- Key issues related to safety include understanding of energetics during thermal runaway, reactivity with electrolytes , abuse tolerance at the cell level, and gas decomposition products generated at these electrodes.
- Previous limited studies on low silicon content (~5%) electrodes clearly indicate the increased heat and gas generation with silicon cells.
- Electrochemical performance of 15% silicon electrodes made to baseline specifications in good agreement to CAMP electrodes.
- Thermodynamic evaluations are ongoing.





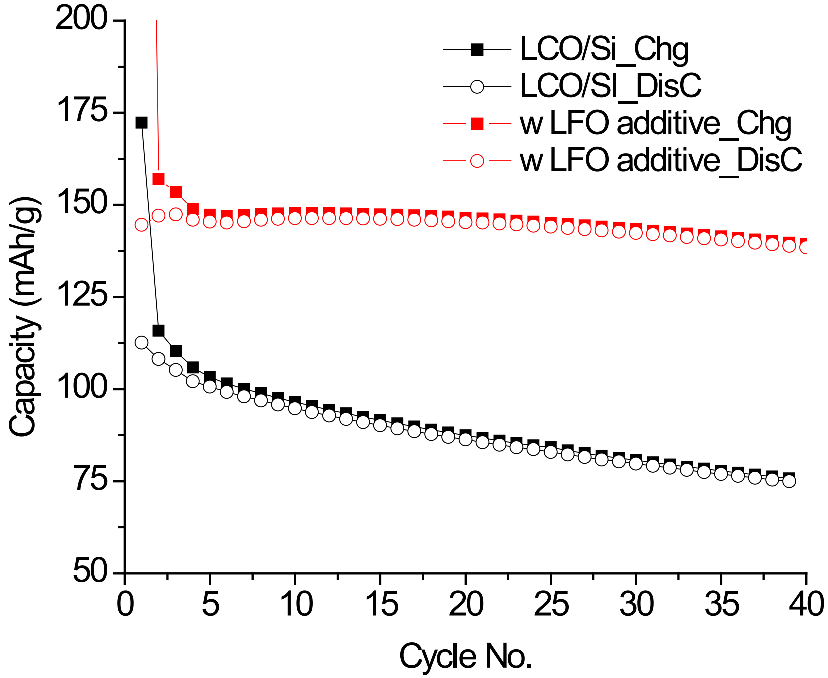
Thermal runaway enthalpy of NMC/Si-C cells is ~10% greater than NMC/Graphite cells



Difference in gas generation attributed to the differences in surface reactivity and surface products generated at the anode/electrolyte interface

ADDING LITHIUM INVENTORY TO COUNTER COULOMBIC EFFICIENCY LOSSES

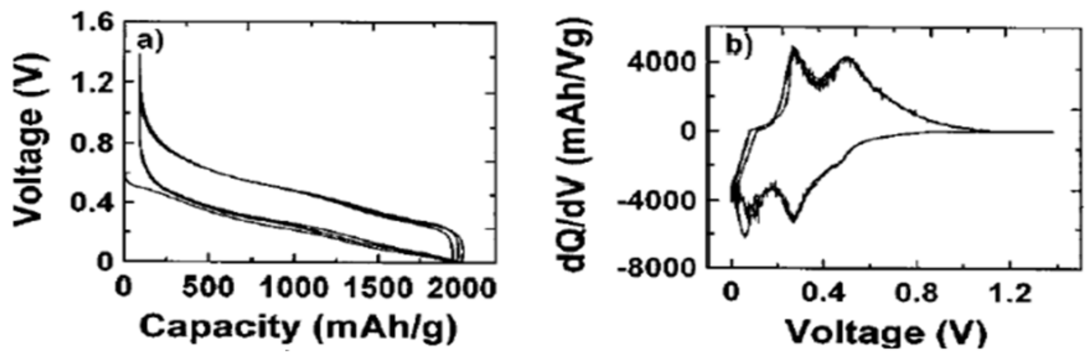
Initial approach using Li_5FeO_4 (LFO) (theoretical 867, actual ~760 mAh/g) as a sacrificial cathode additive



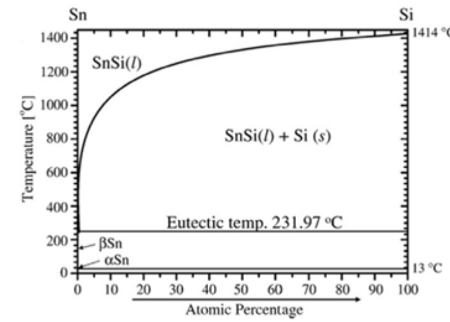
- Sacrificial lithium source additive in positive electrode being implemented.
- Modeling being utilized to predict impact.
- Synthesized new batch of LFO for blending with baseline NMC cathode.
- Other alternatives being considered.
  - Investigate sacrificial lithium species additive introduced via electrolyte
  - Use chemistry to pre-lithiate Si powders or electrodes; test and conduct feedback

DEVELOPMENT OF HIGH ENERGY METALS

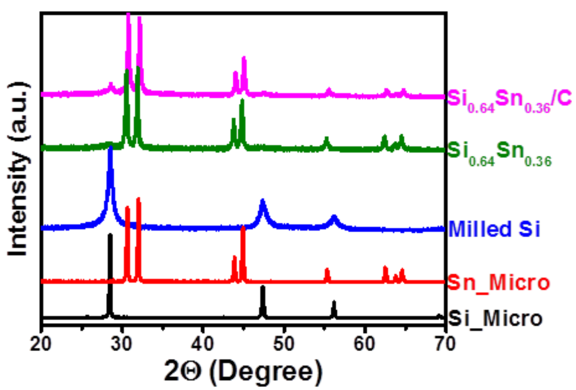
Initial Studies on Amorphous $Si_{0.64}Sn_{0.36}$

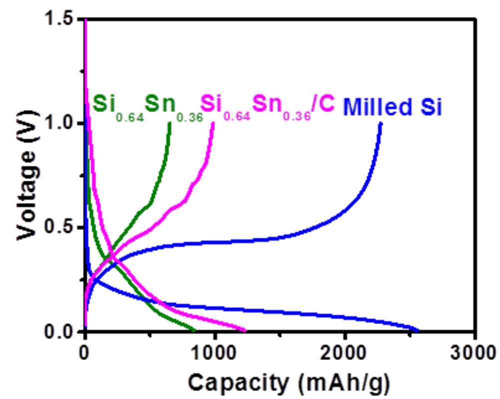


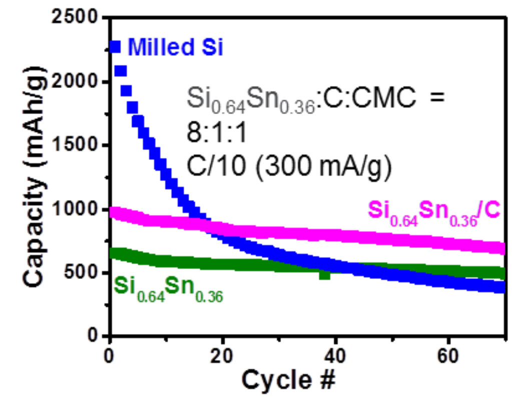
Journal of The Electrochemical Society, **150** (2) A149-A156 (2003)



J. Phys. D: Appl. Phys. **47** (2014) 393001





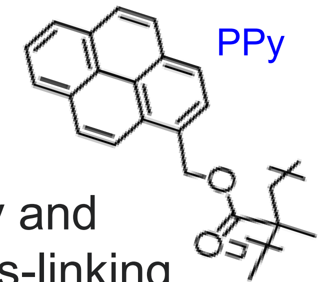


- Amorphous $Si_{0.64}Sn_{0.36}$ thin film exhibits high discharge capacity (>2000 mAh/g) and low irreversible capacity (~100 mAh/g).
- Immiscible gap between Si and Sn, and low melting T of Sn (232 ^{0}C) appear to be the main challenge for $Si_{0.64}Sn_{0.36}$ large-scale synthesis.

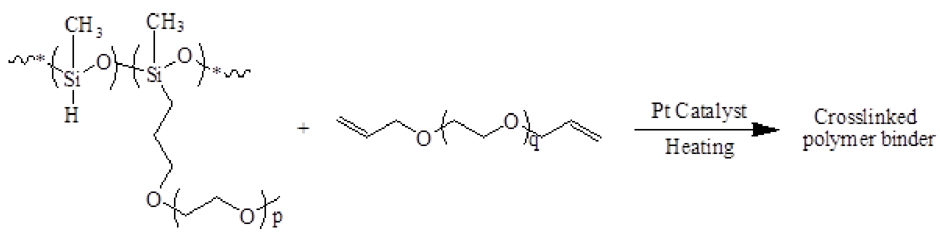
FUNCTIONAL POLYMER BINDER DEVELOPMENT FOR SILICON BASED ELECTRODES

Ideal binders should have excellent chemical stability; exceptional mechanical, flexibility, and adhesive properties; as well as high ionic and electronic conductivity. THERE ARE NO IDEAL BINDERS.

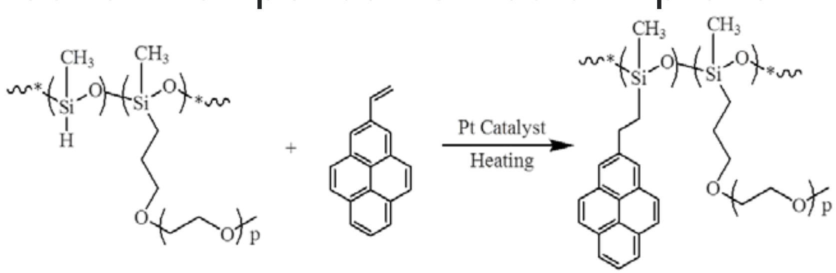
PPy



- Polypyrene (PPy)-based polymers are being studied as functional conductive binders
- Linear siloxanes have many desirable properties such as elasticity and durability but lack adhesion and conductivity. Incorporation of cross-linking network would improve the tensile strength and adhesive properties.



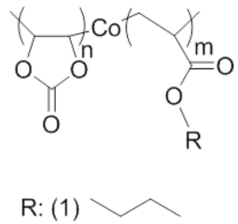
  – Introduction of electron rich pendants would improve the conductivity.

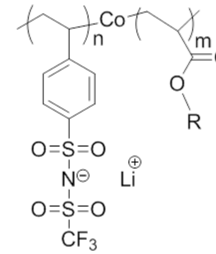


FUNCTIONAL POLYMER BINDER DEVELOPMENT FOR SILICON BASED ELECTRODES

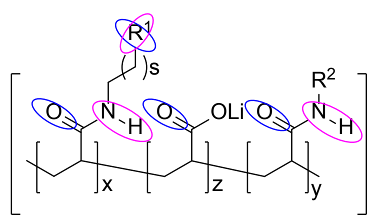
Continued

- A variety of functional polymers are being explored that have desirable characteristics including strong adhesion, ionic conduction and electronic conduction. Examples: Polycarbonate-based polymer binders and Single-ion (Li) conducting polymer binders.





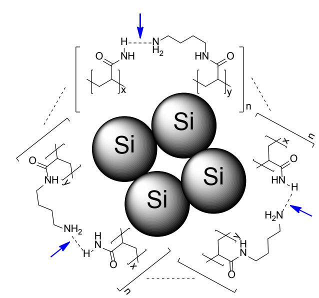
- Acrylate-based, comb- and brush-copolymers bearing hydrogen bond donors and hydrogen bond acceptors in the side chains will afford a flexible, dynamic secondary structure which will adapt to the dynamic size and shape of the anode particles, much like a net surrounding fruit.



hydrogen bond donor and acceptor sites

R^1, R^2 = H, Alk, Ar, N-het, O-het, $CONR_2$, NR^3R^4

R^3, R^4 = H, Alk, COAlk, COAr, $CONR_2$



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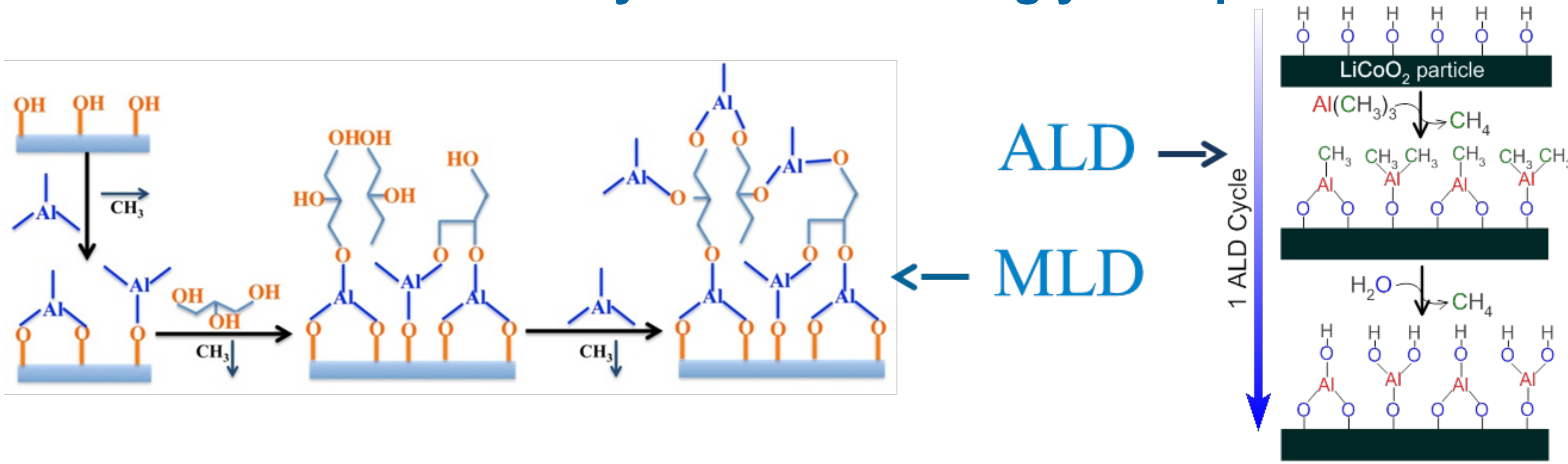
SURFACE MODIFICATION USING MOLECULAR AND ATOMIC LAYER DEPOSITION (MLD & ALD)

Initial MLD studies focus on aluminum-glycerol (AlGL) alkoxide ultrathin films from trimethylaluminium and glycerol precursors.

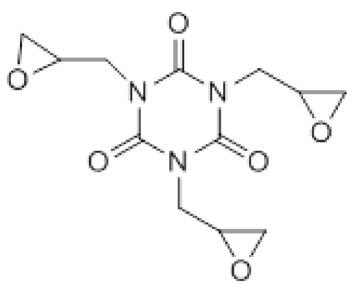


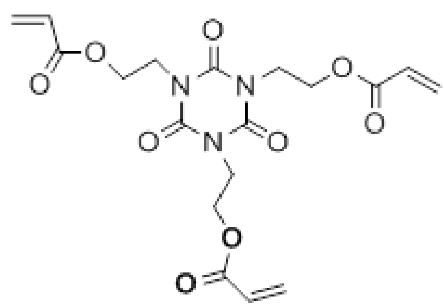
- Advantages of MLD/ALD coatings include conformal and atomic thickness control, especially powerful for 3-D nano complex architectures such as electrodes, and commercially scalable process.
- Developed MLD alkoxide coatings for both silicon nanoparticles and baseline silicon anodes.
- Initial electrochemical studies of coated particles and electrodes in half-cells are promising.

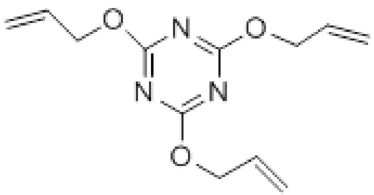
SURFACE MODIFICATION USING PARTICLE COATINGS AND ELECTROLYTE ADDITIVES

Development of Additives and Coatings to Enhance SEI Stability Beyond Fluoroethylene Carbonate (FEC)

- Initiated electrolyte additive study with silane-based molecules
- Began surface treatment of the silicon particles with silane coupling agents
- Initiated screening of SEI additives with flexible linkage and cross-linking groups
  - Long linkages are expected to afford flexibility of the SEI layers
  - Cross-linking groups including epoxy, vinyl, etc, will help to improve the mechanical property of SEI layers

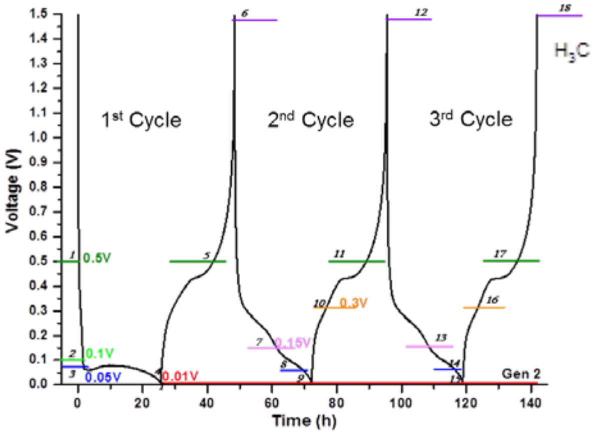


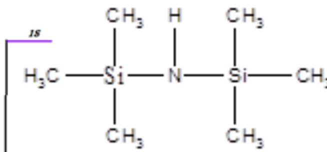




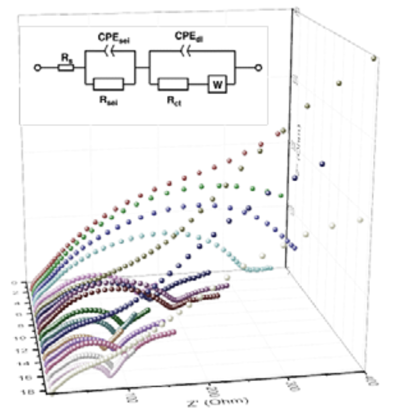
IMPACT OF ADDITIVE ON SILICON ANODE

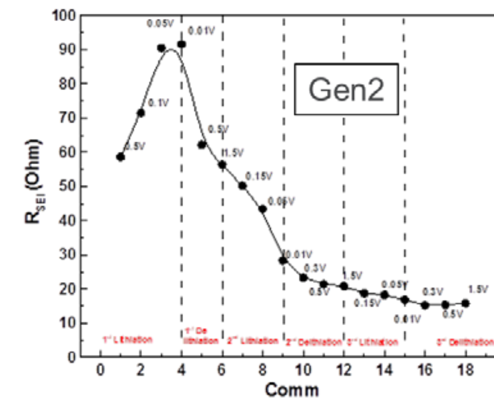
Evolution of SEI Interfacial Impedance During Early Cycling Used as an Indicator of SEI Stability



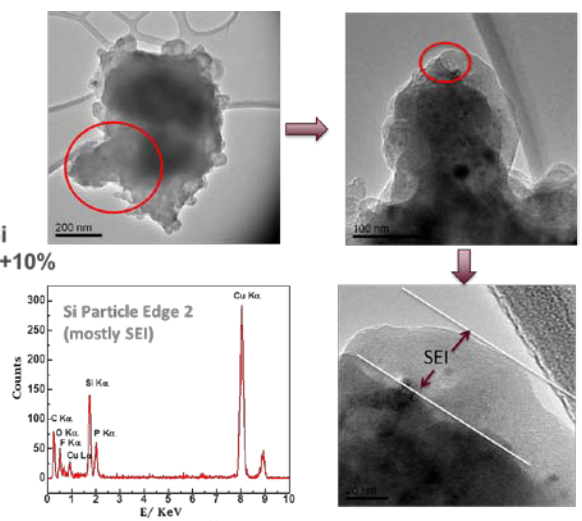


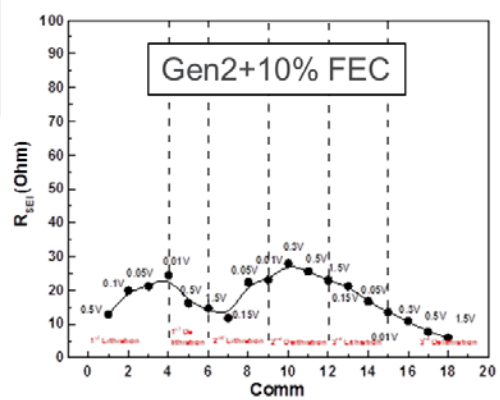
Electrode: Si: Super P: PAA = 2:1:1
Electrolytes: Gen 2 (EC:EMC); Gen 2+10% FEC; Gen2+ 10% FEC+ 0.5% Hexamethyldisilazane

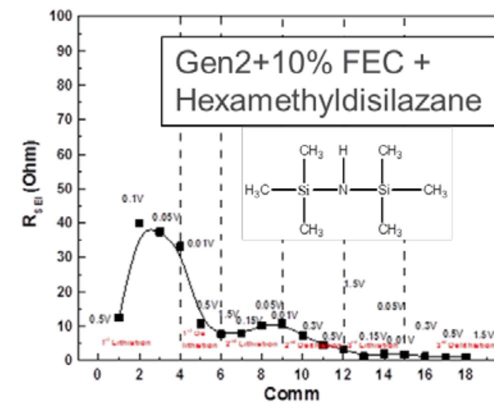




TEM image of Si Anode in Gen2 +10% FEC + Additive







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FUTURE WORK

Future Efforts Focused on Building and Expanding Early Diagnostic and Materials Development Studies

- Explore and study range of available silicon materials to establish new baseline.
- Expand electrochemical and analytical diagnostic studies. Sample highlights:
  - *In-situ* and *ex-situ* micro-Raman imaging
  - EQCM-D to identify surface film properties
  - Soft x-ray microscopy and Nanotomography.
- Further evaluation of safety and abuse tolerance, focusing on determining correlation between material level and full cell level.
- Continue materials development efforts, testing promising candidates in full cells, including:
  - Optimize Li_5FeO_4 as a cathode lithium inventory additive and explore alternative methods.
  - Extend studies on amorphous $Si_{0.64}Sn_{0.36}$
  - Synthesize and examine a range of functional binders.
  - Further explore surface modification studies using molecular and atomic layer deposition, silane-based particle coatings, and electrolyte additives

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SUMMARY

Efforts Focused on Standing Up the Program and Initiating an Extensive Array of Diagnostic and Materials Development Studies

- Adopted electrodes and protocols from CAMP facility for initial baselines.
- Initiated integrated electrochemical and analytical diagnostic studies. Sample highlights:
  - Reference electrode studies
  - NMR spectroscopy investigations
  - Studies on model systems
- Began evaluation of safety and abuse tolerance.
- Initiated materials development efforts. Highlights include:
  - Synthesized Li_5FeO_4 as a cathode additive for a lithium inventory source.
  - Started studies on amorphous $Si_{0.64}Sn_{0.36}$
  - Synthesized a number of functional binders and began evaluation.
  - Began surface modification studies using molecular and atomic layer deposition, silane-based particle coatings, and electrolyte additives

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

This is a new program for fiscal year 2016 and as such it was not reviewed last year.